FINAL SYNOPSIS OF THE Ph.D. THESIS TO BE SUBMITTED TO

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ON THE TOPIC

DEPERTURBATION ANALYSIS OF SOME BANDS OF DIATOMIC ALUMINUM OXIDE MOLECULE

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1. Introduction:

The appearance of AlO molecule in Mira variables and 'M' type of stars is well-known. In recent times it was observed that the flame coming out of rockets produce the compounds of Aluminum and when sunlit, they emit the blue green system of AlO. The emission spectra of this AlO produced in clouds could be photographed and temperatures in upper atmosphere could be calculated. In recent warfare the Aluminized grenades which are exploded in the upper atmosphere can undergo chemiluminescence and fluorescence reaction in the twilight and the bands of all seen AlO is also observed in the spectra of sunspots. Few texts have discussed diatomic the theory of molecules at length [1-8].

In our efforts to investigate AlO the blue green system $B^2\Sigma$-$X^2\Sigma$ system was extensively studied [9] and the rotational structure of some 13 bands was analyzed to yield the accurate constants. The spectra was recorded on a Fourier Transform Spectrometer.

The intensities of the rotational lines of (0,0) band of B-X transition were measured and the rotational temperature was measured [10].

Few, observations eluded in our earlier studies, now are undertaken, which comprises the deperturbation analysis and the reduced potential curve studies of few iso-electronic molecules to AlO.

The Franck-Condon factors and r-centroides of few band systems of AlO were also calculated in the present work. A detailed review of all the papers on AlO was taken [11-36].

2. PERTURBATION STUDIES:

If two energy levels are close together, they perturbs each other either by bringing out the change in the frequencies of expected rotational lines or by showing the anomalous intensity patterns. Sometimes 'displacements' and weakening of the lines may appear simultaneously. This is just like a resonance phenomenon where at particular J value there is a maximum shift from expected position and then it reduces slowly as you go away to either wavelengths. The magnitude of the shift is sometimes even up to 20 cm^{-1} from the normal position. Magnitude of a perturbation depends on the magnitude of a matrix elements W_{12} defined as

$$W_{12} = \int \Psi_1 W \Psi_2 \, \delta\tau$$

Where W is perturbation function. Ψ_1 and Ψ_2 are the eigenfunctions of the two states involved.

3. Selection rules in perturbation:

1) Both states must have same J value i.e. $\Delta J = 0$

2) Both states must be of same multiplicity i.e. $\Delta S = 0$

3) The Λ values of both states must differ by 0 or ±1 i.e. $\Delta\Lambda = 0, \pm 1$

4) Both states should be of same parity and of symmetry i.e. +←→–

   and a←→s.

In case of vibrational levels if two vibrational states belonging to two different electronic states higher energy level goes higher and lower goes lower. Details are given by Hertzberg [5].

4. Perturbation in AlO spectra:

The known electronic states of AlO are $X^2\Sigma^+$, $A^2\Pi^i$, $B^2\Sigma^+$, $C^2\Pi_r$, $D^2\Sigma^+$, $E^2\Delta_i$ and $F^2\Sigma^+$. The $A^2\Pi_i$ state is just 5282 cm^{-1} high from $X^2\Sigma^+$. They perturb each other. The A-X transition gives the band system in IR around 2μ. This $A^2\Pi_i$ state also influences the next excited state $B^2\Sigma^+$ and the spin splitting constant of this state therefore show anomalous behavior. Wherever the bands of $X^2\Sigma^+$ and $A^2\Pi_i$ cross, there the rotational lines get perturbed. Even the band heads of the $A^2\Pi_i$ state of v=4 and of $X^2\Sigma^+$ involving v=9 in various transitions get shifted. These studies are undertaken in the present thesis.

5. The Franck-Condon factors and r-centroids:

The Franck-Condon factors and r-centroids are important entities in molecular spectra as the F-C factors give an idea of the appearance of the bands (intensities) in the spectrum. The F-C factors and r-centroids of A-X, D-X, D-A and D-B systems are calculated for the first time. The F-C factors of B-X, C-X and C-A systems are already reported [37].

6. The Reduced Potential Energy Curve:

The potential energy curves shade the light on the nature of binding and dissociation energy. Many well-known empirical potential functions like Hulbert-Hirschfelder [H-H] [38-39], extended Rydberg [40-41] are supposed to give good fits to RKRV curves. In order to study these, the potential energy curves of the ground states ($^2\Sigma$) of group 5A hydrides are plotted using above potential functions are compared with respective RKRV curves. [42] Similarly the PE curves of the Aluminum halides e.g. AlF, AlCl, AlBr and AlI are also studied.

[43] Where the accurate molecular constants derived from recent FT spectra are used. A novel technique of constructing potential energy curves is suggested by Jenc,[44] in which traditional method of RKRV is not employed. In RKRV method potential energy is plotted against the internuclear separation. In case of RPC, a parameter u which is U/De is plotted against ρ. This ρ is derived from some spectroscopic constant. The minima of RPC is always at (1,1) co-ordinate. Secondly the RPC's of different molecules don't cross each other. Thirdly the RPC's obey some order in their positions. It was thought to see how RPC's behave if the ground electronic state potential curves of isoelectronic molecules to AlO are plotted.

7. Choice of molecules for RPC:

The isoelectronic molecules like MgF, CP, BS, SiN, BeCl, CaO and AlO were chosen. The most recent molecular constants were taken from literature and the RKR curves of their ground states were plotted. The RPC's were also plotted. A combined graph shows the expected results viz.

1) All they have minima at (1,1).
2) They don't cross each other, but the RPC's of BS and CP are very close to each other.

All the RPC's fall between the RPC's of CaH and MgF. The reduced mass increases from CaH (0.9832412) to MgF (10.60470).

8. Organization of the thesis:

Chapter 1 will deal with the chronological development in the field of atomic spectra and molecular spectra. The theory of molecular

spectra is discussed in brief. The motivation of the work will be given.

Chapter 2 will contain the excitation of AlO and essentials of the Fourier Transform Spectroscopy. The salient features, advantages and disadvantages etc over the conventional spectroscopic techniques will discussed.

Chapter 3 will deal with the deperturbation analysis. The precise constants of the $B^2\Sigma^+$ and $X^2\Sigma^+$ states, derived from rotational analysis will be used to the calculate the shifts from expected lines.

Chapter 4 will describe the calculation of F-C factors and r-centroides of A-X, D-X, D-A and D-B systems of AlO.

Chapter 5 will be related to study of potential energy curves. RPC's of few isoelectronic molecules will be calculated and shall be compared with their respective RKRV curves. It was observed that the RPC's obey list of rules. Lastly summary and updated references will be given.

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